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Recovery of Scheelite and Byproduct Sphalerite From Western U.S. Tactite Ores

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UNITED STATES DEPARTMENT OF THE INTERIOR
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RECOVERY OF SCHEELITE AND BYPRODUCT SPHALERITE FROM WESTERN U.S. TACTITE ORES

By J. M. Gomes,[1] A. E. Raddatz,[2] and M. M. Wong[3]

ABSTRACT

Bench-scale flotation tests were conducted on two western tactite ores to study the recovery of tungsten and zinc minerals. The investigation, which is part of the Bureau of Mines ongoing program to develop methods for beneficiating minerals and metals from domestic low-grade ores, demonstrated the feasibility of producing scheelite, sphalerite, and their bulk concentrates. Sphalerite concentrates containing 51 to 53 pct Zn and less than 0.11 pct WO_3 were selectively recovered prior to scheelite flotation. Zinc recovery ranged from 85 to 91 pct. Scheelite concentrates containing 17 to 25 pct WO_3 were then recovered from the ore; tungsten recoveries ranged from 88 to 94 pct. Bulk flotation concentrates containing 84 to 91 pct of the WO_3 and 87 to 95 pct of the zinc also were prepared. More than 98 pct of the WO_3 in a bulk concentrate containing 9 pct WO_3 was extracted by autoclave leaching with a soda solution. The zinc remained in the leached residue.

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INTRODUCTION

The Bureau of Mines is investigating methods for recovering scheelite and associated minerals from Western U.S. tactite ores. The Bureau is concerned with recovering minerals from low-grade domestic resources and with maximizing the recovery of metal values whenever possible. In the western United States, scheelite occurs in contact metamorphic or tactite deposits. In addition to scheelite, the deposits may contain molybdenum, copper, lead, zinc, gold, and silver. The base metals usually occur as sulfide minerals, and gold and silver are usually associated with these sulfide minerals (2).[4] The ores may also contain significant quantities of the nonmetallic minerals, such as fluorite and garnet.

Most western tungsten operations do not recover byproducts. The exception is the 2,000-ton-per-day Pine Creek Mine in Inyo County, Calif. Molybdenum, gold, silver, and copper are recovered in its mill (3). Most tungsten mining operations are small, 100 to 500 tons per day, and operate during periods of high tungsten prices. The recovery of associated mineral and metal values could stabilize the operations during periods of depressed tungsten prices.

The introduction of the soda-autoclave-solvent extraction process for the preparation of ammonium paratungstate (APT) has eliminated the need for preparing 60-pct-WO_3 concentrates (4). Before the APT process, only high-grade concentrates were accepted for processing. With the advent of this process, emphasis was placed on high scheelite recovery and concentrates containing 10 to 20 pct WO_3. The preparation of lower grade WO_3 concentrates permits alternatives for the recovery of byproduct minerals. If the byproduct mineral is insoluble in a soda lixiviant, the WO_3 can be separated from the other minerals and will yield byproduct residue. If the byproduct metal is soluble, selective precipitation or solvent extraction methods may be used to recover the metal.

The objectives of this investigation were to determine potential byproduct metals and minerals in samples from major tungsten deposits in the Western States and to study methods for the recovery of scheelite and byproduct values frome ores containing significant quantities of byproducts.

PRELIMINARY INVESTIGATIONS

The analyses of tactite samples obtained from six tungsten mining districts are shown in table 1. The samples contained the usual skarn minerals--epidote, garnet, and diopside--and quartz, calcite, pyrite, and pyrrhotite.

The major byproduct constituents were sphalerite and fluorspar in the Lincoln County No. 1 ore (L1O) and sphalerite in the Lincoln No. 2 ore (L2O). Molybdenite in the Mineral County, Nev., and Madera County, Calif., samples could also be recovered.

TABLE 1. - Analysis of tactite ores, percent

Source	WO_3	Al_2O_3	CaO	Fe_2O_3	MgO
Madera, Calif.	1.49	10.2	18.8	9.1	2.0
Elko, Nev.....	2.3	4.8	20.3	19.5	2.5
Lincoln, Nev.:					
L1O.....	1.17	5.5	17.9	8.7	1.8
L2O.....	.17	<.2	22.7	5.5	1.2
Mineral, Nev..	.56	4.8	19.3	15.0	2.5
Pershing, Nev.	.60	10.1	25.5	8.2	3.1
	MnO	SiO_2	CaF_2	Zn	Mo
Madera, Calif.	1.2	43.0	0.2	0.01	0.05
Elko, Nev.....	1.8	36.0	.2	<.01	<.01
Lincoln, Nev.:					
L1O.....	2.0	41.0	5.2	2.6	<.01
L2O.....	2.0	46.1	.6	5.7	<.01
Mineral, Nev..	1.8	36.0	.2	<.01	.1
Pershing, Nev.	.7	47.0	.1	<.01	.01

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Bulk sulfide flotation concentrates were recovered from the samples. The analyses of the sulfide concentrates are shown in table 2. The major reason for recovering sulfide concentrates is that most of the potential byproducts occur as sulfide minerals or are associated with the sulfide minerals. In commercial practice, sulfide concentrates are obtained at many scheelite mills because the sulfide minerals are preferentially concentrated with the reagents used in the flotation of scheelite (4-5). The most efficient method for preventing sulfide grade dilution is to selectively recover the sulfide minerals before scheelite flotation.

TABLE 2. - Analysis of sulfide flotation concentrates

Source	Weight, pct	Pct							Oz/ton	
		Bi	Cu	Fe	Mo	Pb	Zn	S	Au	Ag
Madera, Calif.....	1.6	0.01	0.50	33.0	0.70	0.40	0.5	40.5	0.04	1.5
Elko, Nev.....	3	.01	.40	56.0	<.01	<.02	<.05	36.0	.03	Trace
Lincoln, Nev.:										
L10.....	8	.85	.2	19.0	.07	.6	38.0	35.8	Trace	.4
L20.....	14	.01	.05	7.4	<.01	.02	36.5	27.5	.02	.9
Mineral, Nev.....	1.8	.02	.07	26.2	.07	.2	.15	31.0	Trace	1.1
Pershing, Nev.....	.8	.19	.56	32.5	.48	.17	.2	37.2	Trace	1.7

The major minerals in the sulfide concentrates were pyrite and sphalerite. Some concentrates contained minor amounts of pyrrhotite. The L10, which contained scheelite, sphalerite, and fluorite, was selected for further investigation. The L20 was also selected for the recovery of scheelite and sphalerite. The Madera concentrate contained 0.04 oz of gold and 1.5 oz of silver per ton. The Pershing and Mineral concentrates contained 1.7 and 1.1 oz of silver per ton, respectively. The byproduct mineral contents of the Madera, Pershing, and Mineral Counties ores were considered too low to warrant additional studies.

EXPERIMENTAL PROCEDURES

Samples selected for flotation studies were crushed to minus 20 mesh in laboratory cone and roll crushers. The minus 20-mesh ore was reduced to minus 100 mesh by grinding for 1 hr in a laboratory jar mill. The mill charge was 1,000 g of ore and 500 g of water. The flotation experiments were performed in a Denver No. 12[5] laboratory cell. Reno municipal water was used in the experiments. Pulp density was about 33 pct solids, unless specifically stated otherwise. Tungsten and zinc were analyzed by X-ray fluorescence, gold and silver by fire assay, and other elements by atomic absorption or inductively coupled plasma.

EXPERIMENTAL RESULTS

Flotation of Scheelite and Sphalerite

The L10 and L20 contained significant quantities of zinc. The L10 also contained 5.2 pct CaF_2. The selective recovery of scheelite and sphalerite was investigated. The following steps were used and are shown in the flowsheet in figure 1: (1) sulfide flotation to remove pyrite, (2) sphalerite flotation, (3) rougher scheelite

[5]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

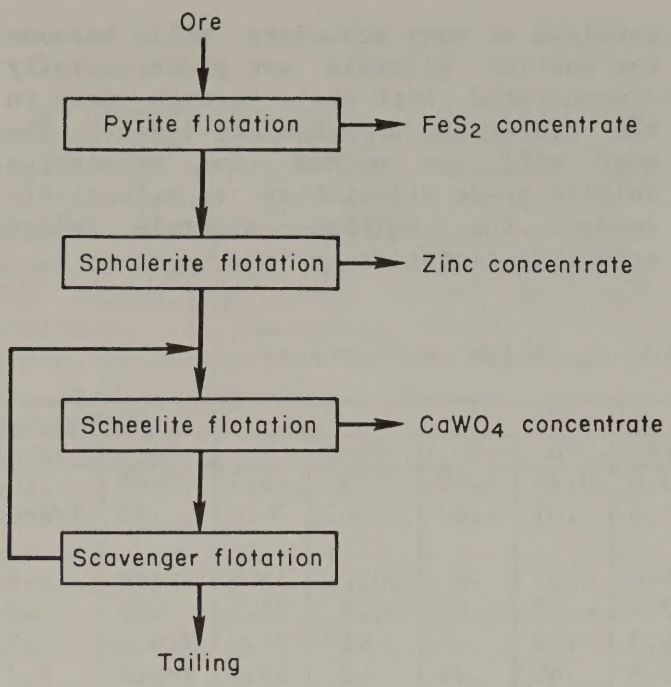

FIGURE 1. - Flotation sequence for Lincoln ores.

flotation, and (4) scavenger scheelite flotation. Since satisfactory results were obtained in the preliminary studies, only a few reagents were investigated for the flotation of pyrite and sphalerite. The investigation indicated that sodium sulfide and copper sulfate used in sphalerite flotation had an adverse effect on scheelite flotation. Therefore, sodium sulfide was eliminated, and copper sulfate was decreased to the minimum quantity necessary for efficient zinc recovery.

Grinding and screening of the ores showed that 50 pct of the fine scheelite and sphalerite grains concentrated in the minus 400-mesh fractions. This is illustrated in table 3, which shows the particle size distribution and WO_3 and Zn distribution in L10 and L20 feeds to flotation.

TABLE 3. - WO_3 and Zn distribution in ground Lincoln ores

Ore and sieve size	Weight, pct	Analysis, pct		Distribution, pct	
		WO_3	Zn	WO_3	Zn
L10:					
Plus 100	2.0	0.41	0.91	0.8	0.7
100 by 150	5.2	.43	1.20	2.2	2.3
150 by 200	10.2	1.1	2.6	10.8	9.8
200 by 270	12.1	1.2	3.0	13.9	13.5
270 by 400	16.2	1.3	3.2	20.2	19.3
Minus 400	54.3	1.0	2.7	52.1	54.4
Total	100.0	NAp	NAp	100.0	100.0
L20:					
Plus 100	3.1	0.09	2.1	1.4	1.1
100 by 150	11.9	.06	3.2	3.5	6.3
150 by 200	11.1	.14	3.9	7.7	7.1
200 by 270	13.0	.14	5.4	9.0	11.6
270 by 400	20.3	.20	7.1	20.1	23.7
Minus 400	40.6	.29	7.5	58.3	50.2
Total	100.0	NAp	NAp	100.0	100.0

NAp Not applicable.

Because of the low WO_3 content of the L20, a preflotation gravity-concentration technique was considered. A heavy mineral concentrate was prepared with a laboratory heavy-liquid separation procedure using Diiodomethane (sp. gr. 3.3). Microprobe and microscopic examinations of the heavy fraction showed that a considerable portion of the scheelite and sphalerite grains were in the 10-μm range, and it contained over 90 pct gangue minerals. Gravity concentration did not appear effective and was rejected.

The conditions and quantities of reagents used for the four flotation steps are shown in table 4. The following reagents were used in sulfide flotation: sodium carbonate for pH adjustment, sodium ethyl and potassium amyl xanthates for sulfide collection, and Dow 250 for a froth control. In the zinc flotation step, copper sulfate was the sphalerite activator, and Z-200 (isopropyl ethyl thiocarbamate) was the collector. In the scheelite flotation step, sodium silicate (grade K) was the silicate mineral depressant, lanolin was the calcite depressant (1), tall oil (FA-2) was the scheelite collector, and Dow 250 was the frother. Other scheelite collectors were investigated, such as oleic acid, Dressinate TX 65-W, and EPG (FA-3), and all yielded similar results to those obtained with the tall oil (FA-2).

TABLE 4. - Flotation conditions and reagents for Lincoln ores[1]

Flotation steps	Conditioning time, min	pH	Reagents	
			Type	Amount, lb/ton
Pyrite.....	5	9.2	Sodium ethyl xanthate.....	0.2
			Potassium amyl xanthate.....	.2
			Dow 250 frother.....	.10
Sphalerite.....	5	9.0	Sodium carbonate.....	4.0
			$CuSO_4$.....	.4
			Isopropyl ethyl thiocarbamate	.2
Rougher scheelite.....	10	9.7	Sodium carbonate.....	2.0
			Dow 250 frother.....	.10
			Na_2SiO_3 (K grade).....	11.0
			Tall oil.....	.60
			Lanolin.....	.50
Scavenger scheelite.....	5	9.6	Dow 250 frother.....	.10
			Tall oil.....	.30

[1]Ores ground for 60 min and with 1.0 lb Na_2CO_3 per ton.

Analyses of flotation products and distributions of metal values are shown in table 5. Photomicrographs of the sphalerite and scheelite concentrates are shown in figure 2. The only minerals identified in the sphalerite concentrate, figure 2A, were sphalerite and pyrite. The sphalerite grains contain approximately 10 pct Fe. The iron content in more than 20 grains was constant. The scheelite concentrate, figure 2B, contains scheelite, calcite, and fluorite and <1 pct quartz and pyrite. The rougher scheelite concentrate prepared from the L10 had the following mineral composition, in percent: scheelite, 31; sphalerite, 6.7; fluorite, 29; and calcite, 12. The remainder was skarn type minerals. The rougher scheelite concentrate obtained from the L20 had the following mineral composition, in percent: scheelite, 21; sphalerite, 43; fluorite, 11; calcite, 13.5; skarn type minerals, 11.5.

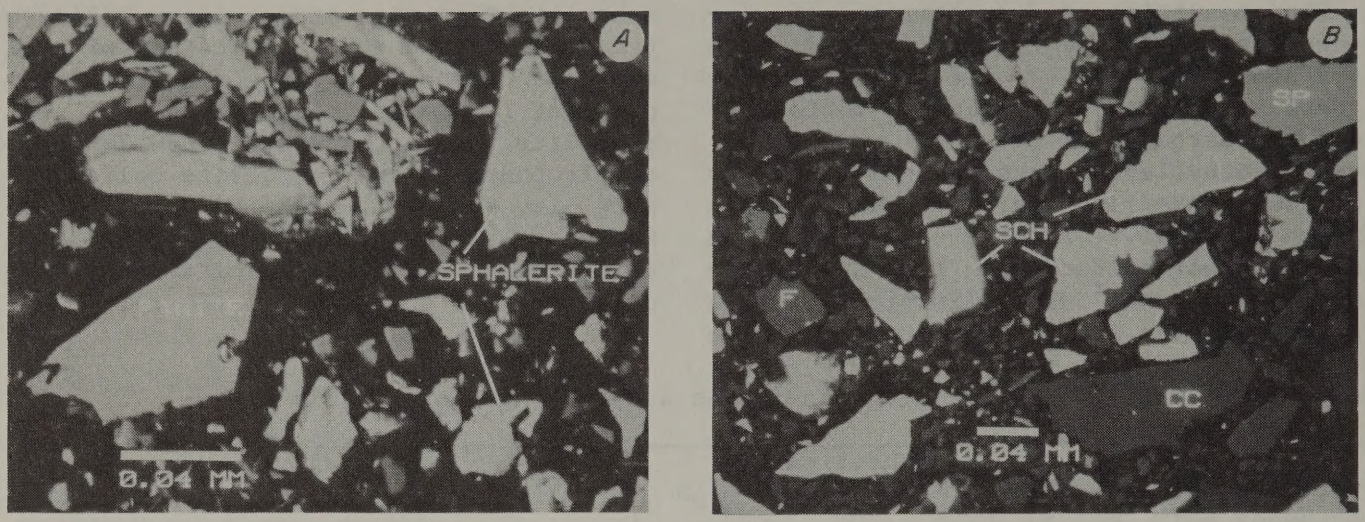

FIGURE 2. - Scheelite and sphalerite concentrates. *A*, Sphalerite concentrate from L10; *B*, scheelite concentrate from L20. SCH–scheelite, CC–calcite, F–fluorspar, and SP–sphalerite.

TABLE 5. - Analysis and distribution of WO_3 and Zn in flotation products

Products	Weight, pct	Analysis, pct		Distribution, pct	
		WO_3	Zn	WO_3	Zn
L10 concentrate:					
Pyrite	2.74	0.36	5.19	1	5
Sphalerite	4.07	.11	53.40	<1	85
Rougher scheelite	3.80	25.00	4.50	88	7
Scavenger scheelite	2.20	3.00	.40	6	<1
Tailing	87.17	.05	.08	4	3
Total	100.0	NAp	NAp	100	100
L20 concentrate:					
Pyrite	1.20	0.01	12.00	0	3
Sphalerite	9.70	.03	51.80	2	91
Rougher scheelite	.75	17.0	29.0	74	4
Scavenger scheelite	.45	5.40	8.80	14	<1
Tailing	87.90	<.02	.11	10	2
Total	100.00	NAp	NAp	100	100

NAp Not applicable.

The sphalerite concentrate prepared from the L10 contained 85 pct of the zinc and <1 pct of the WO_3. The rougher and scavenger scheelite concentrates contained 94 pct of the WO_3 and 7 pct of the zinc. The sphalerite concentrate from the L20 contained 91 pct of the zinc and 2 pct of the WO_3. Eighty-eight percent of the WO_3 and 4 pct of the zinc were recovered in the rougher and scavenger scheelite concentrates. The sphalerite concentrates from the Lincoln ores

contained more than 50 pct Zn and were considered marketable. The scheelite concentrates from the L10 and L20 contained 25 and 17 pct WO_3, respectively, which are acceptable grades for feed to an APT plant.

The effect of pulp density on scheelite and zinc recovery and concentrate grades was investigated with the L10. The results are shown in table 6. The procedure and reagents were the same as those shown in table 4, except that the pulp densities were varied from 28 to 42 pct. Increasing the pulp density from 33 to 42 pct would increase plant capacity by about 25 pct.

TABLE 6. - Effect of pulp density on WO_3 and Zn recoveries

Pulp solids, pct	Scheelite concentrate				Sphalerite concentrate	
	Rougher		Scavenger			
	WO_3, pct	WO_3 recovery, pct	WO_3, pct	WO_3 recovery, pct	Zn, pct	Zn recovery, pct
28	28	77	1	14	31	90
33	25	86	3	6	53	90
38	25	85	4	12	49	88
42	28	79	9	11	46	89

The combined rougher and scavenger WO_3 recoveries ranged from 90 to 97 pct and the zinc recoveries from 88 to 90 pct. The best overall recoveries--WO_3, 92-97 pct, and zinc, 88-90 pct--were obtained at pulp densities of 33 and 38 pct. The scheelite concentrate grades ranged from 25 to 28 pct WO_3. The zinc contents of the sphalerite concentrates ranged from 31 to 53 pct. Increasing the flotation pulp density from 33 to 42 pct did not adversely affect recovery or grade of the scheelite concentrates.

Recovery of Bulk Concentrates

The recovery of a concentrate containing sphalerite and scheelite was investigated because this type of concentrate could be used as feed for an autoclave leaching-solvent extraction process for the preparation of ammonium paratungstate (APT). The WO_3 in the bulk concentrate would be leached with sodium carbonate in an autoclave. The zinc in the residue could be recovered by roasting followed by caustic or acid leaching.

The flotation conditions used to obtain a bulk scheelite-sphalerite concentrate were similar to those shown in table 4. A pyrite concentrate was prepared, and the separate sphalerite flotation step was eliminated. Copper sulfate to activate sphalerite was added with the reagents for the rougher scheelite flotation. The pulp was conditioned 10 min and a bulk concentrate recovered.

The flotation results for the L10 and L20 are shown in table 7. The bulk concentrate prepared from the L10 contained 9.4 pct WO_3 and 20.9 pct Zn, and recoveries of 91 pct of the tungsten and 87 pct of the zinc were obtained. The bulk concentrate from the L20 contained 1.5 pct WO_3 and 46.5 pct Zn, and recoveries were 84 pct WO_3 and 95 pct Zn.

TABLE 7. - Recovery of bulk sphalerite-scheelite concentrates

Products	Weight, pct	Analysis, pct		Distribution, pct	
		WO_3	Zn	WO_3	Zn
L10 concentrate:					
Pyrite.....	3.7	0.50	8.1	2	12
Bulk.....	10.8	9.4	20.9	91	87
Scavenger.....	3.3	1.1	.4	3	<1
Tailing.....	82.2	.05	.04	4	1
Total.....	100.0	NAP	NAp	100.0	100.0
L20 concentrate:					
Pyrite.....	1.7	0.25	10.2	2	3
Bulk.....	11.9	1.50	46.5	84	95
Scavenger.....	1.2	.32	5.3	2	1
Tailing.....	85.2	.03	.10	12	1
Total.....	100.0	NAp	NAp	100.0	100.0

NAp Not applicable.

Sodium Carbonate Leaching of Bulk Concentrates

The L10 concentrate was pressure leached in a sodium carbonate solution, which extracted more than 98 pct of the WO_3. Operating conditions were as follows: 100 g of concentrate, 20 g Na_2CO_3 (400 pct stoichiometric), 300 ml H_2O, and 3 hr at 200° C and approximately 300 psig. Leaching conditions were similar to those used in the commercial sodium carbonate leaching of scheelite. The residue contained 0.25 pct WO_3, 24 pct Zn, 35 pct CaF_2, 20 pct $CaCO_3$, and the remainder, gangue minerals. The pregnant solution containing 29.4 g WO_3 and <0.001 g Zn per liter is suitable for feed to the APT process. The residue was suitable for further processing. The zinc could be extracted by selective leaching and the fluorite beneficiated by flotation.

CONCLUSIONS

Scheelite and sphalerite concentrates were selectively recovered from two complex tactite ores. A sphalerite concentrate containing 85 pct of the zinc and <1 pct of the WO_3 was recovered from the L10, which contained 2.6 pct Zn and 1.17 pct WO_3. Rougher and scavenger scheelite concentrates containing 94 pct of the WO_3 and 7 pct of the zinc were obtained.

A sphalerite concentrate containing 91 pct of the zinc and 2 pct of the WO_3 was obtained from the L20, which contained 5.7 pct Zn and 0.17 pct WO_3. Rougher and scavenger scheelite concentrates containing 88 pct of the WO_3 and 4 pct of the zinc were obtained from the L20.

The WO_3 contents of the L10 and L20 rougher scheelite concentrates were 25 and 17 pct, respectively, and would be acceptable feed for a soda leaching-solvent extraction process and preparation of APT. The zinc contents of the L10 and L20 sphalerite concentrates were 53.4 and 51.8 pct, respectively, and were acceptable market products.

Bulk flotation concentrates containing 9.4 pct WO_3 and 20.9 pct Zn, and 1.5 pct WO_3 and 46.5 pct Zn, were recovered from the L10 and L20, respectively. The zinc recoveries in the bulk concentrates were 87 and 95 pct, and the WO_3 recoveries were 91 and 84 pct (for L10 and L20, respectively).

The WO_3 was selectively extracted from the concentrate containing 9.4 pct WO_3 by the soda autoclave-leaching technique. The pregnant solution contained 29.4 g WO_3 and <0.001 g Zn per liter, and the residue contained 24 pct Zn. The bulk concentrates are suitable feed for preparation of APT by the soda leaching-solvent extraction process.

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